

CLAIMS

1. A layerwise optical moulding process which uses a non-coherent source of radiation and wherein the photocurable composition comprises at least two curable components:

5 (i) at least 70%, preferably at least 80%, more preferably at least 85% by weight of the total curable components in the composition is a first component that is photocurable and that is such that, when cured in the presence of a photocuring initiator by exposure to UV radiation having an energy of 30 mJ/cm^2 , at least 90% by weight of the component is cured within 50 milliseconds; and

10 (ii) at least 5%, preferably at most 30%, preferably at most 20%, preferably at most 15% by weight of the total curable components in the composition is a second component that results in the composition, on curing, shrinking, in a linear direction, by less than 3% in length and preferably that results in the composition having, after cure, a T_g of greater than 50°C , preferably at least 100°C and more preferably at least 120°C .

- 15 2 A process as claimed in claim 1, wherein at least 90% by weight of the first component is cured within 50 milliseconds, when the first component is cured in the presence of a photocuring initiator by exposure to UV radiation having an energy of 20 mJ/cm^2 (more preferably 10 mJ/cm^2).

- 20 3 A process as claimed in claim 1, wherein the first component comprises one or more materials selected from the group consisting of:

25 (a)(h) an acrylate, e.g. mono, bis and higher order functionality acrylate, or a mixture thereof, the acrylate preferably comprising at least one acrylate having a functionality of 2 or more, or

(i) an amine base proliferation system comprising an amine photoinitiator, a base amplifier and an anionically curable material, e.g. a glycidyl epoxy or an acrylate or an anhydride having a functionality of at least 2, or

(c)(j) an acid amplified system comprising at least one cationically photocurable material, for example an epoxy (e.g. a cycloaliphatic epoxy), a cationic photocuring initiator, e.g. Tri-aryl sulfonium SbF_6 salts, and an acid amplifier, e.g. a tosylated compound and

5 (d)(k) a polymer chain, e.g. a polyester, polyether, polycarbonate, polybutadiene, polyurethane, polyalkane, or polysiloxane, having 2 or more functional photoinitiation groups that, on exposure to radiation, can form reactive groups that react with curable components in the composition to incorporate the said polymer chain into the cured composition, the polymer chain preferably being a flexible
10 and/or toughening chain.

4 A process as claimed in any one of claims 1 to 3, wherein the second component comprises one or more material selected from of the group consisting of:

15 (a)(l) a methacrylate, e.g. mono, bis or higher order functionality methacrylate or a mixture thereof, and preferably comprising at least one methacrylate with a functionality of at least 2,

(b)(m) a compound having at least one terminal -SH, -NH or -OH group, e.g. an oligomeric liquid polysulphides, a mercaptan monomer, or a reactive alkane bearing at least one amine, hydroxy or thio terminal group, and

20 (c)(n) (i) an isocyanate, optionally blended with a latent polyol, e.g. derived from an epoxy, or a polyamine, e.g. derived from a blocked amine, for example an aliphatic amine derived from a carbamate, , or

(ii) a hybrid bearing an isocyanate group and a urethane group,

25 (iii) an epoxy, e.g. a cycloaliphatic epoxy or a glycidyl epoxy, optionally with an acid amplifier, and

(iv) an oxetane, a furan or an ortho-spiro compound.

5. A process as claimed in claim 4, wherein the second component comprises a polythiol having two or more thiol groups per molecule, e.g. a polythiol obtained by esterification of a polyol with an α - or β -mercaptocarboxylic acid (such as thioglycolic acid, or β -mercaptopropionic acid), or pentaerythritol tetramercaptoacetate or pentaerythritol tetrakis- β -mercaptopropionate (PETMP).
6. A process as claimed in any one of claims 1 to 5, wherein the photocurable composition also contains one or more flexibiliser or toughener, (e.g. (a)(v) a hydroxyl-containing compounds, (for example a polyester, polyether, polycarbonate or a polyurethane), or (b)(vi) a thiol or amino counterpart of the hydroxyl versions), or a reactive rubber / elastomeric compound, (e.g. a polybutadiene having epoxy, acrylyl, amino, hydroxy, thiol, or amino functional groups, or a core shell toughener with reactive or compatible surface or a linear or cyclic polysiloxane having epoxy, acrylyl, hydroxyl, thiol, or amino functional groups).
7. An optical moulding composition comprising, in weight percent:
- (a)(o) at least two curable components:
- (i) a first component in an amount of at least 80%, preferably –at least 85% by weight, based on the total weight of the curable components in the composition, the first component being photocurable and such that, when cured in the presence of a photocuring initiator by exposure to UV radiation having an energy of 30 mJ/cm^2 , at least 90% by weight of the component is cured within 100 milliseconds, preferably within 50 milliseconds; and
- (ii) a curable second component in an amount of at least 5% by weight of the total curable components in the composition, the second component being a compound having at least one terminal thiol (-SH) group, e.g. an oligomeric liquid polysulphides, a mercaptan monomer, a polythiol having two or more thiol groups per molecule, (e.g. a polythiol obtained by esterification of a polyol with an α - or β -mercaptocarboxylic acid, such as thioglycolic

acid, or β -mercaptopropionic acid, or a pentaerythritol tetramercaptoacetate or pentaerythritol tetrakis- β -mercaptopropionate (PETMP)).

(b)(p) 0 to 10%, preferably 1 to 10%, of a cationic photoinitiator,

(c)(q) 0 to 10, preferably 0.01 to 10% of a radical photoinitiator,

5 (d)(r) 0 to 5%, preferably 0.001 to 5% of a stabilizer against premature curing prior to use in the process, and

(e)(s) 0 to 20% of auxiliary materials, e.g. fillers, particularly sub micron particles, 'nano size' fillers, e.g. siloxane particles, silica particles, nano-clays, nano-metals.

10 8. A composition as claimed in claim 7, wherein at least 90% by weight of the first component is cured within 50 milliseconds, when the first component is cured in the presence of a photocuring initiator by exposure to UV radiation having an energy of 20 mJ/cm² (more preferably 10mJ/cm²).

15 9. A composition as claimed in claim 7 or claim 8, wherein the first component comprises one or more materials selected from the group consisting of:

(a)(t) an acrylate, e.g. mono, bis and higher order functionality acrylate, or a mixture thereof, the acrylate preferably comprising at least one acrylate having a functionality of 2 or more,

20 (b)(u) an amine base proliferation system comprising an amine photoinitiator and a photo-polybase amplificater, and an anionically photocurable material, e.g. an acrylate having a functionality of at least 2, or

(c)(v) an acid amplified system comprising at least one cationically photocurable material, for example an epoxy (e.g. a cycloaliphatic epoxy), a cationic photocuring initiator, e.g. a tri-aryl sulfonium SbF₆ salts, and an acid amplifier, e.g. a tosylated compound.

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10. A composition as claimed in any one of claims 7 to 9, wherein the photocurable composition also contains
- 1 to 10% by weight of one or more flexibilisers or tougheners, e.g. (a)(w) a hydroxyl-containing compounds, (for example a polyester, polyether, polycarbonate or a polyurethane), or (b)(x) a thiol or amino counterpart of the hydroxyl versions), or a reactive rubber / elastomeric compound, (e.g. a polybutadiene having epoxy, acrylyl, amino, hydroxy, thiol, or amino functional groups , or a linear or cyclic polysiloxane having epoxy, acrylyl, hydroxyl, thiol, or amino functional groups).
- 10 11. A composition as claimed in any one of claims 7 to 10, wherein the first component is an acrylate.
12. A composition as claimed in any one of claims 7 to 11, wherein the first component includes a carbon-carbon double bond, e.g. an acrylate, and the ratio of double bonds to thio groups in the composition is 10:1 to 2:1, e.g. 9:1 to 4:1, for example 8:1 to 5:1.